

JC07 Rec'd PCT/PTO 21 MAR 2002

| | | | | | |
|--|--|---|--|---|--|
| FORM PTO-1390 (REV 12-2001) | | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | | ATTORNEY'S DOCKET NUMBER 12707P04US | |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | | | U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/088849 | |
| INTERNATIONAL APPLICATION NO. PCT/EP00/09230 | | INTERNATIONAL FILING DATE 21 September 2000 | | PRIORITY DATE CLAIMED 22 September 1999 | |
| TITLE OF INVENTION Al_2O_3/SiC NANOCOMPOSITE ABRASIVE GRAINS, METHOD FOR PRODUCING THEM AND THEIR USE | | | | | |
| APPLICANT(S) FOR DO/EO/US Paul MOLTGEN, Pirmin WILHELM | | | | | |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: | | | | | |
| 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). | | | | | |
| Items 11 to 20 below concern document(s) or information included: | | | | | |
| 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input checked="" type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information: Data Sheet | | | | | |

| | | | | | |
|--|--|--|--|--|--|
| 10/088849 <small>U.S. APPLICATION NO. (If known) See 37 CFR 1.53</small> | | <small>INTERNATIONAL APPLICATION NO.</small> | | <small>ATTORNEY'S DOCKET NUMBER</small> 12707P04US | |
|--|--|--|--|--|--|

| | | | | | |
|--|---------------------|---------------------|-------------|-----------------------------------|--------|
| 21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | CALCULATIONS PTO USE ONLY | |
| | | | | \$ 890 | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ 130 | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | \$ | |
| Total claims | 29 - 20 = | 9 | x \$18.00 | \$ 162 | |
| Independent claims | 3 - 3 = | 0 | x \$84.00 | \$ | |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) <u>yes</u> | | | | + \$280.00 | \$ 280 |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ 1,462 | |
| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | | | \$ | |
| SUBTOTAL = | | | | \$ | |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ | |
| TOTAL NATIONAL FEE = | | | | \$ | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | | | \$ | |
| TOTAL FEES ENCLOSED = | | | | \$ 1,462 | |
| | | | | Amount to be refunded: | \$ |
| | | | | charged: | \$ |

a. ☒ A check in the amount of \$ 1,462 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.

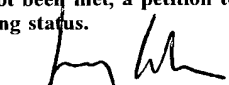
c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 03-241.0A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Jerry Cohen, Esq.
 Perkins, Smith & Cohen, LLP
 One Beacon Street
 Boston, MA 02108
 (617) 854-4000


 SIGNATURE
Jerry COHEN
 NAME
20,522
 REGISTRATION NUMBER

12707 P04US
JC/mej
03/21/02

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Paul MOELTGEN, Pirmin WILHELM
For: Al₂O₃/SiC NANOCOMPOSITE ABRASIVE GRAINS, METHOD FOR
PRODUCING THEM AND THEIR USE

Perkins, Smith & Cohen, LLP
One Beacon Street
Boston, Massachusetts 02108
(617) 854-4000

To: Assistant Commissioner for Patents
Washington, DC 20231

Box PCT

PRELIMINARY AMENDMENT MADE UPON U.S. NATIONAL PHASE ENTRY

Please amend certain claims in the above-identified application as follows:

-- 1. (amended) Method for the production of Al₂O₃/SiC nanocomposite abrasive grains, characterized by the fact that an aluminum-oxide containing sol is mixed with sinter additives and SiC nanoparticles and subsequently gelled, dried, calcined and sintered the sintering being conducted by heating the mixture in the range between 1300°C and 1600°C.

--

-- 4. (amended) Method according to [one or several] either of Claims 1 [through 3] or 2, [characterized by the fact that] wherein prior to the gelling, sintering additives in the form of crystallization seeds, crystal growth inhibitors and/or other modifying components that influence the sintering process are added.--

-- 6. (amended) Method according to [one or several] either of Claims 1 [through 5] or 2, [characterized by the fact that] wherein the gelling of the suspensions occurs by increasing or decreasing the pH value; through aging; the addition of electrolytes; increased temperature; and/or concentrating the solution. --

-- 7. (amended) Method according to [one or several] either of Claims 1 [through 6] or 2,

Amended claim 1 was considered in the International Preliminary Examination report of 14 December 2001 (the claim having been submitted to the IPEA on 27 November 2001).

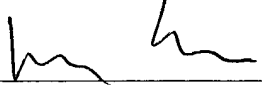
If sums are owed due to claim adjustments, please charge (or debit) Deposit Account 03-2410.

Respectfully submitted,

Paul Moeltgen, Pirmin Wilhelm, Applicants

Dated: March 21, 2002

By:



Jerry Cohen
Reg. No. 20,522
Attorney for Applicants

Appendix A (clean net claims)

1. Method for the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains, characterized by the fact that an aluminum-oxide containing sol is mixed with sinter additives and SiC nanoparticles and subsequently gelled, dried, calcined and sintered the sintering being conducted by heating the mixture in the range between 1300°C and 1600°C .
4. Method according to either of Claims 1 or 2, wherein that prior to the gelling, sintering additives in the form of crystallization seeds, crystal growth inhibitors and/or other modifying components that influence the sintering process are added.
6. Method according to either of Claims 1 or 2, wherein the gelling of the suspensions occurs by increasing or decreasing the pH value; through aging; the addition of electrolytes; increased temperature; and/or concentrating the solution. -
7. Method according to either of Claims 1 or 2, wherein drying of the gel is carried out in a temperature range between 50°C and 120°C , with subsequent calcination between 500°C and 800°C , and sintering in a temperature range between 1300°C and 1600°C .
10. Method according to either of Claims 1 or 2, wherein comminution to the desired grain size is done before or after sintering.
13. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to either of Claims 11 or 12, wherein the SiC particles are predominantly present intragranularly in the Al_2O_3 matrix.
14. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to either of Claims 11 or 12, wherein the Al_2O_3 crystals of the matrix show mean diameters of between $0.2\text{ }\mu\text{m}$ and $20\text{ }\mu\text{m}$.
15. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to either of Claims 11 or 12, wherein the Al_2O_3 matrix has a submicron structure and a mean particle size of $< 1\text{ }\mu\text{m}$, preferably $< 0.5\text{ }\mu\text{m}$.
19. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to either of Claims 16 through 18, wherein the coarse Al_2O_3 crystals have a length/width ratio of between 2:1 and 10:1, preferably between 4:1 and 6:1.

10/088849

1010 Rec'd PCT/PTO 21 MAR 2002

3/p/12TS

WO 01/2121547

PCT/EP00/09230

Description

Al₂O₃/SiC nanocomposite abrasive grains, a method for their production, and their use

The invention at hand concerns sintered Al₂O₃/SiC nanocomposite abrasive grains in accordance with the characterizing clause of Claim 11; a process for their production in accordance with the characterizing clause of Claim 1; as well as their use as abrasives.

Abrasive grains on Al₂O₃ basis are processed industrially in large quantities into abrasives due to their great hardness, chemical inertness and high temperature resistance. In addition to melting corundum that can be produced relatively cost-effectively in the arc furnace, sinter corundums obtained via a ceramic or chemical route have been used more extensively in recent times for certain areas of application. The advantage of sinter corundums, in terms of abrasive engineering, is based on their microcrystalline structure which in turn leads to a particular wear mechanism of the abrasive grain during the grinding process. Especially in applications that require high pressures [against the work piece] such as, e.g., the processing of special steels, hardened steels or hard-to-chip alloys, the abrasion output can be markedly increased through the use of sinter corundums. The sinter corundum with its microcrystalline structure is considerably more wear resistant for those applications than the melting corundum with its macrocrystalline structure. In addition, during the grinding with microcrystalline corundums, small segments break off, forming new cutting edges that in turn intervene in the grinding process. Such a self-sharpening of the grain does not take place in the case of macrocrystalline melting corundums because the cracks that are caused by the mechanical stress of the grain can no longer be deflected, but rather

proceed through the entire grain along the crystal plane surface through the entire grain, thereby leading to the destruction of the abrasive grain

During the use of microcrystalline sinter abrasive grains, it can be observed in many applications that during the grinding process the abrasive grain, with comparable hardness and density, behaves the more favorably the more delicately the structure is developed.

Particularly fine structures may be obtained via sol/gel processes in which e.g. super-finely dispersed aluminum oxide monohydrate of the Boehmite type is used as a base material which – after having been dissolved as a colloid – is processed into a gel which is then further processed into a compact and dense α Al_2O_3 sinter body via a drying, calcination and sintering phase. Subsequently, it is processed into an abrasive grain. The advantage of the so/gel method for the production of corundums with microcrystalline structure lies in the fact that reactive base materials with very small components are used and the resulting green bodies can be condensed at relatively low sintering temperatures which favors the formation of a fine structure.

In EP-B-0 152 768, microcrystalline corundums are described that are produced using the sol/gel technique with the addition of characteristic crystallization seeds at sintering temperatures of approximately 1,400 °C and whose primary crystallites have a diameter that is predominantly, or in their entirety, less than 1 μm .

Due to the low sintering temperatures and through the addition of crystallization seeds, it is possible to severely restrict crystal growth during the sintering process. Even finer structures, with simultaneous high density and hardness, are described in EP-B-0 408 771.

According to EP-B-0 408 771 corundum grains with a median crystallite size of < 0.2 μm are obtained via the sol/gel technique as well, with the addition of particularly fine crystallization seeds while maintaining a special temperature and sintering program in which the temperature range between 900 and 1,100 °C is passed within 90 seconds, the material is brought to a maximum temperature that should not exceed 1,300 °C, with subsequent tight sintering below that maximum temperature in the range between 1,000 and 1,300 °C. The

If one wishes to obtain a structure of the finest possible crystals, one can also use, in addition to the use of crystallization seeds, sintering additives that hinder the growth of crystals or accelerate the sintering process and thereby indirectly restrict the formation of larger crystals. The influence of individual additives to the sintering process and the crystal growth during the sintering of Al_2O_3 is summarized in the “*Journal of the American Ceramic Society Vol 39, No 10, 1956*” Of the numerous patents that describe the use off sintering additives or combinations of sintering additives and crystallization seeds for the production of abrasive grains via the sol/gel route, only a few examples will be described in the following. EP-B-0 024 099 describes the addition of spinels or, respectively, of raw materials that are turned into spinels during the course of the production process. EP-B-0 024 099 describes the use of α Fe_2O_3 crystallization seeds in combination with at least one modified component from the group of oxides of magnesium, zinc, cobalt, nickel, zirconium, hafnium, chromium and/or titanium. EP-B-0 373 765 describes – also in combination with α Fe_2O_3 seeds – yttrium and neodymium compounds in addition to the oxides named above, as additional modifying components. The abrasive grains produced in accordance with the above-named methods have advantages for certain uses as compared to the state of the art.

The multiplicity of the various Al_2O_3 sintering grains can be explained by the fact that the grinding itself is an extremely multifarious process during which the material that is being processed as well as the processing conditions (pressure [against the material], cooling, and others) can be greatly varied. Thus, the most dissimilar materials (varying types of steel, alloys and metals, plastics, wood, stone, ceramic and many more are processed under the most varying conditions, depending on the objective (surface quality, material abrasion, and others). The demands made on the abrasive grain to be used vary accordingly, meaning that the usability and efficacy of an abrasive grain can not be characterized by factors such as hardness,

density, and crystallite structure alone. Other criteria such as chemical inertness, heat conductivity, oxidation and temperature resistance, toughness, and others, play an important role as well, depending on the use.

Additional variables of the grinding process are bonding and the specification of the abrasive agent which can be further variegated through the use of additives (auxiliary abrasive agents, pore formers, et al.).

Thus, in the case of abrasive grains produced via the sol/gel route, it was attempted in the past not only to increase the efficacy via the fineness of the crystal structure but also to obtain specific favorable properties for certain uses via dopings. EP-B-0 228 856 describes the addition of yttrium that is added – e.g. in the form of an yttrium salt with an easily volatile anion (nitrate, acetate, et al.) - to the α aluminum monohydrate during the sol/gel process and that reacts with the aluminum oxide to yield yttrium aluminum garnet ($3Y_2O_3 - 5Al_2O_3$). This material shows special advantages in the processing of stainless steel, titanium, nickel alloys, Aluminum and other, hard-to-chip alloys, but also with ordinary construction steel. Obviously, the imbedding of garnet crystals provide the abrasive grain with a particular wear resistance for those application which is then reflected in a high abrasion output. In addition to the Y_2O_3 or, respectively, its raw materials, the addition of crystallization seeds and/or other sintering additives is described. In EP-B-0 293 164, the addition of rare earths from the praseodymium, samarium, ytterbium, neodymium, lanthanum, gadolinium, cerium, dysprosium, erbium group and/or combinations of several members from this group is described as well. In this process, the rare earths form hexagonal aluminates with Al_2O_3 which, as imbeddings in the Al_2O_3 matrix, obviously increase the wear resistance of the abrasive grain even more. EP-B-0 368 837 describes abrasive grains whose toughness is increased through the formation of whisker-like crystals that are obtained through the addition of cerium compounds. The sol/gel methods also yields composites that are described in DE-A-196 07 709 and that differ from the aforementioned compounds in that in addition to the Al_2O_3 matrix at least two

additional discontinuous structural components are present that differ from each other in the mean particle size by at least a factor of 10. In EP-B-0 4 91 184, composites on the basis of Al_2O_3 are described that feature imbeddings of isometric hard substances that are larger by at least a factor of 10 than the primary crystals that the matrix is constructed of.

All of the aforementioned processes and materials are based on sol/gel technology that makes it possible – with the simultaneous use of sintering additives – to realize a very fine, preferably submicron crystallite structure. Also, the abrasive grains are often tailor-made and optimized for certain areas of utilization through additional dopings.

In general, abrasive agents or, respectively, abrasive grains can be simply divided into two large groups. Corundum belongs, besides SiC, to the so-called conventional abrasive agents that have been known for a long time and that are produced, and used, cost-effectively in large quantities. In addition, recently one has been finding more and more often the so-called super abrasives, such as diamond and cubic boron nitride, whose production costs are a thousand fold to ten thousand fold higher as compared to the production costs of conventional abrasive grains, but that provide an extremely favorable price/performance ratio due to their efficacy, the reduced machine down-time related therewith, and the low consumption of the abrasive agent itself or, respectively, the increase of the per-piece number per time unit and abrasive agent.

However, the use of super abrasives requires specialized machinery which in turn requires the corresponding investments, and that limits the range of uses for high-performance abrasive agents even more.

Therefore, one of the main objectives in the development of new abrasive grains is to obtain an abrasive grain that can be used in conventional machines but whose performance level lies between conventional abrasive agents and the super abrasives. This has been achieved, in part, with the aforementioned sol/gel corundums that can be used in many grinding operations at a very favorable price/performance ratio. However, the sol/gel corundums must be

grouped closer to the conventional abrasive grain types not only because of their production costs but also because of their performance potential, and therefore they are more suitable to replace the conventional corundum types in grinding operations that do not justify the use of super abrasives.

Therefore, the task of the invention at hand is to make available abrasive grains with an even better performance potential - as compared with the aforementioned state of the art - as well as a process for their production. In accordance with the invention, this task is solved through the characteristics of Claim 11 or, respectively, of Claim 1. The sub-claims concern advantageous models of the invention. Claim 20 concerns a suitable utilization of the abrasive grains obtained in accordance with the invention.

The term nanocomposite which found entry into ceramics approximately 10 years ago denotes systems that consist of at least two different solid phases of which at last one phase features particle sizes in the nanometer range.

$\text{Al}_2\text{O}_3/\text{SiC}$ composites in which SiC particles are built into an Al_2O_3 matrix for reinforcement purposes are described in EP-B-0 311 289 and are provided for use in engine or turbine engineering, e.g. as structural ceramics. In this respect, the diameter of the SiC particles whose share in the composite amounts to between 2 and 10 mol % should be below $0.5 \mu\text{m}$ while the Al_2O_3 particles should not exceed $5 \mu\text{m}$. These materials in which the SiC particles are dispersed in the Al_2O_3 particles are characterized by an extraordinary bending strength and toughness and can be used as structure ceramic in engine engineering due to their good high-temperature properties.

Similar $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites that contrast with the known whisker, fiber or platelet-reinforced composite materials through their good high-temperature properties and oxidation resistance are described by Niihara in the *Journal of the Ceramic Society of Japan* 99 [10] 974 - 982 (1991). The influence of small-sized SiC particles on the growth of grains and the sintering behavior of the Al_2O_3 matrix is

described by Stearns, Zhao and Harmer in the *Journal of the European Ceramic Society* 10 (1992) 473 – 477. The mechanical properties of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites are examined by Zhao, Stearns, Harmer, Chan, Miller and Cook in the *Journal of the American Ceramic Society* 76 [2] 503 – 510 1993. Nanocomposites produced via the sol/gel route are described by the authors Xu, Nakahira and Niihara in the *Journal of the Ceramic Society of Japan*, 1994, 102, 312 – 315.

While the places in the literature quoted above mostly refer to composites with SiC portions of > 2 mol %, the mechanical properties of hot-pressed $\text{Al}_2\text{O}_3/\text{SiC}$ composites with low portions of SiC are listed in an article by authors Wilhelm and Wruss in the *cfi/Ber. DGK* 75, 40 – 44 (1998). In addition to the places in the literature quoted above, the $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites have been described in numerous other publications that have been largely summarized in an overview by Sternizke in the *Journal of the European Ceramic Society* 17 (1997) 1061 – 1082. In that article the suspicion is vented, too, that $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites could close the gap between conventional abrasive agents and super abrasives. In contrast to this presumption, however, almost all publications mentioned in that article and the material properties quoted therefrom expressly refer to the use as a structural ceramic. Thus, e.g., the microstructures, thermodynamic stability, density, hardness, breaking strength, fracture toughness, the wear behavior and the creep rate are all mentioned. All those values are certain to play a role in the grinding process as well, however without allowing, by themselves, a valid statement about the suitability of any material as an abrasive grain. For example, great hardness is certainly a basic requirement for a material to be used as an abrasive grain. However, as the example of B_4C shows that is often quoted in expert circles and that has never found widespread use as an abrasive grain in spite of its great hardness due to its insufficient chemical and thermal constancy and its high brittleness, a sum of properties must be considered in order to recognize the suitability as an abrasive agent. Other hard substances that range in their hardness values between conventional abrasives and super abrasives also could not succeed as abrasive grains because they lack additional properties such as toughness, thermal and chemical stability or other prerequisites.

Therefore it is worth trying to find an independent measuring method and measuring magnitude that permit a direct statement about the suitability of a material as an abrasive grain. In practice, the so-called single-grain test (Illustration 1: single-grain scratch test) has proved more and more successful in recent years in which a single abrasive grain is examined under conditions as realistic as possible, simulated after the grinding process. The test device is a retooled surface grinding machine on which a scratch disk is mounted on the grinding spindle in lieu of the grinding disk. The scratch disk that is made, for practical reasons, of a relatively light and easy-to-work material (e.g.

aluminum) features on its circumference a holding device with an abrasive grain soldered onto it. During the scratching phase itself the supporting table with the work piece attached to it moves in direction x against the rotation direction under the rotating scratching disk. Because of a pre-set feed motion in direction y, the abrasive grain that protrudes beyond the circumference of the disk generates with each revolution a scratch trace in the work piece. With increasing scratch length or, respectively, scratching time, the scratch depth and the scratch cross section decrease due to grain wear until the grain tip has been worn off by the feed motion amount in direction y and no longer leaves a trace. The scratch traces can be scanned with a surface measuring device and then be evaluated. The measuring principle is shown in Illustrations 1 and 2 and will be explained in the following by means of the reference numbers.

Illustration 1 shows the theoretical design of the test stand with the scratching disk (1) and the scratching grain (2), the movable axles (3, 4, 5) in directions x, y, and z, the work piece (6), the support table (7) and the grinding spindle head (8). For the measuring itself, standard conditions must be defined for the cutting speed v_c , the work piece speed v_w , and the feed motion a_c , that are preferably adapted to the grinding operation for which one wishes to use the abrasive grain later. In addition, the work piece material and the use of a cooling lubricant (9) must be determined.

The evaluation principle can be seen in the curves for various abrasive grain types shown as examples (III 2) in which the scratch cross section A_{Rn}/A_{R0} is outlined against the scratch length l_R . In this context, A_{R0} is the scratch cross section after the first intervention, and A_{Rn} the scratch cross section after n mm of scratch length.

The performance factor LF_{25} for the single grain results from the intersection of the characteristic curve for the individual grain type with the ordinate after a scratch length of 25 mm and corresponds to the change of the scratch cross section A_{Rn}/A_{25} . The performance factor is expressed in % relative to the theoretical case that no abrasion of the grain occurs and $A_{R25} = A_{R0}$. The evaluation after a scratch length of

25 mm was chosen because in the typical course of the curve the decisive first and steep section of the curve during which the grain is under the most stress has been concluded. This section which also comes relatively close to the actual grinding process with regard to the feed motion permits a very good statement about the performance potential of an abrasive grain. In the further course, the curves flatten since the grains are now stressed less due to the reduction in the feed motion and thus wear off less rapidly. In order to obtain a representative result for a grinding granulation, at least 20 grains of a grain type should be measured and the abrasion curve should be formed from the mean values of the individual measuring points.

The single-grain scratch test thus permits – quite consistently with the results obtained in practice – to evaluate the suitability of an abrasive grain in which all values relevant for the grinding process, such as hardness, toughness, density, resistance, creeping speed, thermal and chemical resistance, crystallite structure, et al., flow indirectly into the total, without certain properties or, respectively, certain property combinations, having to be explicitly known or recognized and needing to be taken into account. For all properties, however, certain minimum requirements must be met for a material to be considered as an abrasive grain. Thus, e.g., a material whose hardness is clearly below the usual hardness for abrasive agents would never be suitable for grinding even if all other properties were outstanding.

Surprisingly, for $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites with SiC portions under 5 mol % that were produced via a direct sol/gel route with the addition of crystallization seeds, performance factors were found in accordance with the method described above that are clearly above the performance factors found thus far in the case of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites. The performance factors of the nanocomposites according to the invention are also above the values of the known pure or doped sol/gel corundums and thus between the conventional abrasive grains and the super abrasives in the target area.

In contrast with the known $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites that are produced by blending the basic substances and subsequent condensing

(e.g. through hot pressing, pressure-less sintering or hot isostatic pressing) and sintering, the production of the abrasive grains according to the invention proceeds in hydrochemical fashion via a direct sol/gel route with the use of crystallization seeds. Xu, Nakahira and Niihara describe in their article in the *Journal of the Ceramic Society of Japan*, 1994, 102, 312 – 315 the use of the sol/gel technology in the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites. However, they use the technology only in order to achieve the most homogeneous possible blend of the nano powders via an upstream colloidal solution of the particles. The sol is subsequently processed, through drying and calcination, into a homogeneous blend of ultra fine Al_2O_3 and SiC powders that are then hot-pressed – in analogy with conventional powder technology – under nitrogen at a pressure of 30 MPa and a temperature of 1,600 °C.

Due to the isolation of the powder as an interim product and subsequent conventional processing in terms of powder engineering, certain advantages of the sol/gel method that are important for the production of an abrasive grain are lost. The properties in terms of grinding engineering of a composite produced via the above-mentioned method therefore correspond to those of the aforementioned nanocomposite. In addition, there are economic aspects because cost-effective mass production on an industrial scale can not be realized via a hot-pressing method.

In the direct sol/gel method according to the invention for the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites, on the other hand, an Al_2O_3 sol is first produced in the usual manner. As solid components for the aluminum oxide containing sol, micro-dispersed aluminum oxide monohydrate of the Boehmite type, aluminum alkoxides, aluminum halogenides and/or aluminum nitrate are suitable that are dispersed with the aid of a disperser, a strong stirrer, or through the use of ultrasound. The solid contents of the suspension preferably lies between 5 and 60 weight %. Nanoscaled SiC is then added to this suspension, likewise preferably in the form a suspension in order to achieve the most homogeneous possible distribution, between 0.1 and < 5 mol %, preferably in the area of 0.3 and 2.5 mol % relative to the aluminum

contents of the mixture calculated as $\text{Al}_2\text{O}_3/\text{SiC}$. It is of course possible, too, to stir SiC as a solid into the described suspension. As the examples in Table 3 show, especially good results are obtained with comparatively small amounts of SiC. As an SiC basis, most finely ground SiC powder obtained via the Acheson process, or nanopowders produced through thermal or laser-supported gas phase reactions or various plasma methods, are suitable.

In order to favorably influence the later sintering process sintering additives in the form of crystallization seeds, crystallization growth inhibitors and/or other modifying components may be added prior to gelling. For this purpose, all known sintering additives for Al_2O_3 are suitable, e.g. the spinel-forming oxides of Co, Mg, Ni, and Zn, the oxides of Ce, Cu, B, Ba, Hf, K, Li, Nb, Si, Sr, Ti, Y, Zr, or the rare earths or, respectively, their precursors, and the oxides with corundum-like structure such as Fe_2O_3 , Cr_2O_3 , Al_2O_3 , or others that act as crystallization seeds. In order to obtain certain properties of the abrasive grain, combinations of the above may, of course, be used as well.

Preferably, the Al_2O_3 sol is treated with an aqueous suspension of superfinely ground $\alpha\text{-Al}_2\text{O}_3$ particles prior to the addition of SiC. The maximum particle size of the $\alpha\text{-Al}_2\text{O}_3$ particles that serve as crystallization seeds is below μm , preferably below $0.2\ \mu\text{m}$. The amount of seed material to be used depends on the particle size and lies between 0.5 and 10 weight % relative to the Al_2O_3 contents of the end product. Since it depends on the number of seeds, in addition to the fineness, even very small weight amounts of superfine seeds will suffice to promote the sintering process.

The prepared suspension is then heated to the boiling point and expediently gelled through the addition of acid. Here, too, it is possible again to apply as an alternative any other type of gelling (aging, addition of electrolyte, temperature increase, concentration of the suspension, at al.) Drying of the gel (after cooling off) is carried out within a temperature range between $50\ ^\circ\text{C}$ and $120\ ^\circ\text{C}$. Subsequently, calcination occurs in a temperature range between $500\ ^\circ\text{C}$ and $800\ ^\circ\text{C}$.

in order to evaporate the residual water and the acid. After calcination, the composites are present as green bodies with diameters of up to several millimeters, and are then sintered. The advantage of direct compression lie particularly in the high sintering activity of the dried and calcinated green bodies in which the original materials are already bound to each other chemically, with the compression and solidification to the finished composite thus proceeding considerably more effectively and favorably.

This process and thus the product quality may be further improved through the additional use of sintering additives or, respectively, crystallization seeds. The sintering of the calcined gel preferably occurs at temperatures between 1,300 °C and 1,600 °C, preferably under inert conditions (e.g. a nitrogen atmosphere), and particularly advantageously in a gastight rotary oven in order to realize the fastest possible heating of the product and a short sintering time which has a particularly favorable effect on the structure and thus on the efficacy of the abrasive grain. Alternatively, any other known oven type may be used that allows fast heating rates and high temperatures. Since the sintering occurs very fast, processing it is even possible in a vacuum or in an oxidizing atmosphere since the largest portion of the SiC nanoparticles are imbedded in the matrix and are thus protected from oxidation.

Comminution to the desired granulation may occur before or after sintering with the usual comminution aggregates. Preparing the calcinated gel in its green state is advantageous since after sintering considerably more energy must be expended on comminution of the then dense and hard composite material.

During sintering, the nanoscaled SiC acts as crystal growth inhibitor for the Al_2O_3 matrix, but at the same time delays the condensing of the green body, making it necessary to use comparatively – as compared with a sol/gel material on pure aluminum oxide basis - high sintering temperatures in order to achieve sufficient condensation of the material during which step not inconsiderable crystal growth may occur. For example, large crystals occur already at approximately 1,400 °C in

Surprisingly, it was then found that the abrasion output of the nanocomposite abrasive grain according to the invention is particularly high when a certain portion of coarse crystals with lengths of up to 20 μm and a mean diameter of $> 2 \mu\text{m}$, preferably $> 5 \mu\text{m}$, is present in the matrix. The abrasion output lies clearly above that of the finely structured pure sol/gel Al_2O_3 abrasive grains whose mean crystallite size is commonly $0.2 - 0.3 \mu\text{m}$ and in which all crystals are present in the sub micron range, preferably in the range below $0.4 \mu\text{m}$. This is all the more surprising since in expert circles it has generally been known that the abrasion output of sinter corundums with increasingly fine structure - particularly in the d_{50} range under $0.5 \mu\text{m}$ - increases drastically.

As examples 1 – 6 and comparison examples 7 – 11 which describe the influence of sinter conditions on the structure and the efficacy of sinter corundum show, the output curve of the $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite follows a non-linear course with a maximum at a sintering temperature between 1,400 °C – 1,450 °C. The first coarsely crystalline and columnar crystals occur in the matrix within this temperature range with a holding time of 30 minutes. The coarse Al_2O_3 crystals preferably have an oblong shape, with a length/width ratio of between 2:1 and 10:1, particularly preferably between 4:1 and 6:1. Typical images of the matrix with coarse-crystalline imbeddings are reproduced as electron-microscopic photos in Illustrations 3 and 4 on page 19. Below 1,400 °C, a purely submicron structure occurs, with all particles being present in the range of $< 1 \mu\text{m}$, preferably $< 0.5 \mu\text{m}$. The output potential of these materials lies also above that of pure state-of-the-art sol/gel corundums, but surprisingly below the materials with coarse-crystalline imbeddings obtained in the abovementioned temperature

range. The output curve goes down again at still higher temperatures which bring about an increased occurrence of coarse crystals.

However, even at sintering temperatures of 1,500 °C with high portions of coarse crystals, grinding performances are achieved that are on the level of the best pure sol/gel corundums. In contrast, with the pure sol/gel corundums an almost linear course of the output potential can be discerned in accordance with the fineness of the structure, and only in the submicron range, at a mean crystallite size d_{50} of $< 0.4 \mu\text{m}$, are good performances achieved.

Obviously, the coarse crystallites in the nanocomposites cause some kind of structural strengthening that has a positive effect on the wear behavior of the grain and compensates not only for the expected performance decrease caused by grain growth but also provides the abrasive grain, in combination with the imbedded SiC nanoparticles, with a clear performance increase.

By way of the examples in Table 4 it can be seen that the product improvement through the imbedding of SiC particles is limited not only to SiC nanopowder, but also that outstanding abrasive performances can be achieved with grains that show relatively coarse SiC embeddings. However, the trend is unambiguous that the abrasive performance is the better the finer the SiC powders are. Initially, for commercial reasons and for reasons of availability, in the production of the abrasive grain according to the invention, the powders listed in the examples that were obtained through extremely fine grinding of industrial SiC produced via the Acheson method were used exclusively *[this sentence is ungrammatical and/or incomplete in the German original]* However, one may assume that the abovementioned trend will continue when even finer powders are being used.

The SiC particles in the case of the nanocomposites according to the invention may be arranged intragranularly – in the Al_2O_3 matrix particles – as well as intergranularly – at the grain borders between the Al_2O_3 particles - and it can be observed that the smaller particles are preferably integrated in intragranular fashion. The question of what

In the following, the invention will be explained by way of examples; this does not constitute any limitation of the invention.

Examples 1 – 6

Suspension A (Boehmite Sol)

10 kg of pseudo-boehmite (Disperal, firm of Condea) are dispersed with the use of a dispergator (type Megatron MT 1-90, firm of Kinematica) in 50 ml of distilled water whose pH value was adjusted to 2.4. Approximately 300 ml of a 50% α - Al_2O_3 -containing Keim-Slurry with a maximum particle size of $d_{\max} = 0.4 \mu\text{m}$ that was obtained through wet-grinding and subsequent centrifugation of a fine-particled α - Al_2O_3 powder (CS400M, firm of Martinswerk) is added, again with the use of a dispergator. Following the addition of the Keim-Slurry, there are approximately 2 weight % of Al_2O_3 crystallization seeds in the sol.

Suspension B (SiC Suspension)

1.5 g of a 50% aqueous polyethylene imine suspension (firm of Fuka) is added to 600 ml distilled water, stirring vigorously. Subsequently, 30 g of nanoscaled SiC (UF 45, firm of H. C. Starck) is stirred into the diluted suspension.

Suspension B is added to the Boehmite/sol suspension (Suspension A) while stirring, and the pH value of the mixture is adjusted to 1.8 with the aid of nitric acid. Subsequently, the mixture is heated to 95 °C, stirring constantly, and gelling is initiated by adding additional nitric acid drop by drop. After cooling off, the gel is dried at 85 °C in the drying chamber. The dried gel is pre-crushed to a particle size of less than 5 mm and then calcined at approximately 500 °C.

In examples 1 – 6, only the sintering temperatures were varied. In Table 1, the measured hardness values, performance factors and crystallite structures are listed as a function of the sintering conditions

Table 1: Examples 1 – 6

| Example | Sintering Program* | Hardness (HV _{0.2}) | Crystallite Structure (d ₃₀) | LF ₂₅ % |
|---------|---------------------------------|-------------------------------|--|--------------------|
| 1 | 1300 / N ₂ / 60 / 30 | 11.3 GPa | < 0.4 μm | 23 |
| 2 | 1350 / N ₂ / 60 / 30 | 13.3 GPa | < 0.4 μm | 29 |
| 3 | 1380 / N ₂ / 60 / 30 | 19.8 GPa | < 0.4 μm | 73 |
| 4 | 1400 / N ₂ / 60 / 30 | 22.9 GPa | 1 μm | 85 |
| 5 | 1450 / N ₂ / 60 / 30 | 20.7 GPa | 5 - 10 μm | 83 |
| 6 | 1500 / N ₂ / 60 / 30 | 20.1 GPa | 10 - 20 μm | 70 |

* Sintering Program =

sintering temperature (°C) / oven atmosphere / heating rate (°C/min) / holding time (min)

Comparison Examples 7 – 11 (without SiC Embeddings)

10 kg of pseudo-Boehmite (Disperal, firm of Condea) are dispersed with the use of a dispergator (type Megatron MT 1-90, firm of Kinematica) in 50 ml of distilled water whose pH value was adjusted to 2.4. Approximately 300 ml of a 50% α Al₂O₃-containing Keim-Slurry with a maximum particle size of d_{max} = 0.4 μm that was obtained through wet-grinding and subsequent centrifugation of a fine-particle α Al₂O₃ powder (CS400M, firm of Martinswerk) is added, again with the use of a dispergator. Following the addition of the Keim-Slurry, there are approximately 2 weight % of Al₂O₃ crystallization seeds in the sol

The pH value of the mixture is adjusted to 1.8 with the aid of nitric acid. Subsequently, the mixture is heated to 95 °C, stirring constantly, and gelling is initiated by adding additional nitric acid drop by drop. After cooling off, the gel is dried at 85 °C in the drying chamber. The dried gel is pre-crushed to a particle size of less than 5 mm and then calcined at approximately 500 °C.

In comparison examples 7 - 11, too, only the sintering temperatures were varied. Table 2 shows the measured hardness values, performance factors and crystallite structures as a function of the sintering conditions.

Table 1: Examples 1 – 6

| Example | Sintering Program* | Hardness (HV _{0.2}) | Crystallite Structure (d ₅₀) | LF _{25%} |
|---------|---------------------------------|-------------------------------|--|-------------------|
| 7 | 1240 / N ₂ / 60 / 30 | 19.7 GPa | 0.2 – 0.3 μm | 75 |
| 8 | 1300 / N ₂ / 60 / 30 | 22.4 GPa | 1 μm | 63 |
| 9 | 1350 / N ₂ / 60 / 30 | 23.1 GPa | 1 - 5 μm | 60 |
| 10 | 1400 / N ₂ / 60 / 30 | 21.6 GPa | 3 - 7 μm | 49 |
| 11 | 1450 / N ₂ / 60 / 30 | 20.6 GPa | 5 - 10 μm | 40 |

* Sintering Program =
sintering temperature (°C) / oven atmosphere / heating rate (°C/min) / holding
time (min)

Example 12

The production of Example 12 occurs analogously to Examples 1 – 6. However, 75 g of nanoscaled SiC UF45 were utilized.

Example 13

Production occurred analogously to Example 12. Instead of 75 g, 150 g nanoscaled SiC UF45 were used. Table 3 shows the performance factors as a function of SiC concentration.

Table 13: Examples 4, 12, and 13

| Example | Sintering Program | Hardness (HV _{0.2}) | SiC Portion (mol %) | LF ₂₅ (%) |
|---------|---------------------------------|-------------------------------|---------------------|----------------------|
| 4 | 1400 / N ₂ / 60 / 30 | 22.9 GPa | 1.0 | 85 |
| 12 | 1400 / N ₂ / 60 / 30 | 22.4 GPa | 2.5 | 59 |
| 13 | 1400 / N ₂ / 60 / 30 | 23.1 GPa | 5.0 | 37 |

Example 14

Production of Example 14 occurred analogously to Example 4. Instead of SiC UF45, the somewhat coarser SiC UF25 (firm of H.C. Starck) was used.

Sintering was done at a temperature of 1400 °C in a nitrogen atmosphere. The heating rate was 60 °C per minute, and the holding time was at 30 minutes.

Example 15

Production of Example 15 occurred analogously to Example 14. Instead of SiC UF25, the coarser SiC UF15 (firm of H.C. Starck) was used.

Comparison Example 16

Production of Example 16 occurred analogously to Example 15. Instead of SiC UF15, an SiC P1000 (firm of Elektroschmelzwerk Kempten) was used.

Comparison Example 17

Production of Example 17 occurred analogously to Example 16. Instead of SiC P1000, an SiC P600 (firm of Elektroschmelzwerk Kempten) was used.

Table 4 shows the performance factor of the nanocomposite as a function of the particle size of the embedded SiC's

Table 4 Examples 4, 15 – 18

| Example | SiC | Mean Particle Size d_{50} | Hardness (HV _{0.2}) | LF ₂₅ (%) |
|---------|-------|-----------------------------|-------------------------------|----------------------|
| 4 | UF45 | 300 nm | 19.7 GPa | 85 |
| 14 | UF25 | 500 nm | 22.4 GPa | 82 |
| 15 | UF15 | 600 nm | 23.1 GPa | 77 |
| 16 | P1000 | 18 μ m | 21.6 GPa | 73 |
| 17 | P600 | 26 μ m | 23.3 GPa | 58 |

Abrasion Tests

In addition to the scratching test, a few selected examples were subjected to an abrasion test on an abrasive belt. The results of the tests are summarized in Table 5.

Table 5: Abrasion Tests (Belt Grinders)

| Abrasive Grain | Type of Steel | | | |
|----------------|---------------|------------|----------------|------------|
| | Turbine Steel | | Titanium Alloy | |
| | Abrasion (g) | Output (%) | Abrasion (g) | Output (%) |
| Example 4 | 1096 | 145 | 127 | 176 |
| Example 5 | 994 | 131 | 109 | 151 |
| Example 14 | 1023 | 135 | 112 | 155 |
| Example 15 | 843 | 111 | 85 | 118 |

| | | | | |
|--------------------------------|-----|-----|----|-----|
| Example 7 | 781 | 103 | 68 | 94 |
| <hr/> | | | | |
| commercial sol/gel corundum | 757 | 100 | 72 | 100 |
| melt corundum | 320 | 42 | 23 | 32 |

Claims

1. Method for the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains,

characterized by the fact that an aluminum-oxide containing sol is mixed with SiC nanoparticles and subsequently gelled, dried, calcined and sintered.

2. Method according to Claim 1,

characterized by the fact that the aluminum-oxide containing sol contains as a solid component superfinely dispersed aluminum oxide monohydrate of the Boehmite type, aluminum alkoxides, aluminum halogenides and/or aluminum nitrate.

3. Method according to either Claim 1 or Claim 2,

characterized by the fact that the addition of the SiC nanoparticles is done in an amount of between 0.1 and < 5 mol %, preferably in the range of 0.3 and 2.5 mol % relative to the aluminum contents of the mixture, calculated as Al_2O_3 .

4. Method according to one or several of Claims 1 through 3,

characterized by the fact that prior to the gelling, sintering additives in the form of crystallization seeds, crystal growth inhibitors and/or other modifying components that influence the sintering process are added.

5. Method according to Claim 4,

characterized by the fact that fine-particled α aluminum oxide is used as crystallization seed.

6. Method according to one or several of Claims 1 through 5,

characterized by the fact that the gelling of the suspensions occurs by increasing or decreasing the pH value; through aging; the addition of electrolytes; increased temperature; and/or concentrating the solution.

7. Method according to one or several of Claims 1 through 6,

characterized by the fact that drying of the gel is carried out in a temperature range between 50 °C and 120 °C, with subsequent calcination between 500 °C and 800 °C, and sintering in a temperature range between 1300 °C and 1600 °C.

8. Method according to Claim 7,

characterized by the fact that sintering is done in a temperature range between 1380 °C and 1500 °C.

9. Method according to [Claim] 7,

characterized by the fact that sintering is carried out under inert conditions

10 Method according to one or several of Claims 1 through 9,

characterized by the fact that comminution to the desired grain size is done before or after sintering.

11. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain with a hardness of > 16 GPa, a density of $> 95\%$ of the theory, and an SiC portion of between 0.1 and < 5 mol %, relative to the Al_2O_3 matrix,

characterized by the fact that the SiC particles are present in the Al_2O_3 matrix as well as intragranularly and the abrasive grain shows a performance factor $\text{LF}_{25} > 75\%$ in the single-grain scratch test.

12. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to Claim 11,

characterized by the fact that the SiC portion preferably amounts to between 0.3 and < 2.5 mol %, relative to the Al_2O_3 matrix.

13. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to one of Claims 11 or 12,

characterized by the fact that the SiC particles are predominantly present intragranularly in the Al_2O_3 matrix.

14. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to one or several of Claims 11 through 13,

characterized by the fact that the Al_2O_3 crystals of the matrix show mean diameters of between $0.2\ \mu\text{m}$ and $20\ \mu\text{m}$.

15. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grain according to one or several of Claims 11 through 13,

20. Utilization of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains according to one or several of Claims 11 – 19 for the production of grinding belts and grinding disks.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro



(43) Internationales Veröffentlichungsdatum
29. März 2001 (29.03.2001)

PCT

(10) Internationale Veröffentlichungsnummer
WO 01/21547 A1

(51) Internationale Patentklassifikation: C04B 35/117,
35/624, C09K 3/14

WILHELM, Pirmin [DE/DE]; Fridolin-Lauber-Str. 18,
79725 Laufenburg-Binzgen (DE).

(21) Internationales Aktenzeichen: PCT/EP00/09230

(74) Anwalt: NEUNERT, Peter; Westphal, Mussnug & Part-
ner, Waldstr. 33, 78048 VS-Villingen (DE).

(22) Internationales Anmeldedatum:
21. September 2000 (21.09.2000)

(81) Bestimmungsstaaten (national): CA, JP, US.

(25) Einreichungssprache: Deutsch

(84) Bestimmungsstaaten (regional): europäisches Patent (AT,
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE).

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
199 45 335.7 22. September 1999 (22.09.1999) DE

Veröffentlicht:
— Mit internationalem Recherchenbericht.
— Vor Ablauf der für Änderungen der Ansprüche geltenden
Frist; Veröffentlichung wird wiederholt, falls Änderungen
eintreffen.

(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme
von US): TREIBACHER SCHLEIFMITTEL GMBH
[DE/DE]; Ferroweg 1, 79725 Laufenburg (DE).

Zur Erklärung der Zweibuchstaben-Codes, und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): MÖLTGEN, Paul
[DE/DE]; Steigmattstrasse 2, 79725 Laufenburg (DE).

WO 01/21547 A1

(54) Title: $\text{Al}_2\text{O}_3/\text{SiC}$ NANOCOMPOSITE ABRASIVE GRAINS, METHOD FOR PRODUCING THEM AND THEIR USE

(54) Bezeichnung: $\text{Al}_2\text{O}_3/\text{SiC}$ -NANOKOMPOSIT-SCHLEIFKÖRNER, VERFAHREN ZU IHRER HERSTELLUNG SOWIE
IHRE VERWENDUNG

(57) Abstract: The invention relates to a method for producing $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains. SiC nanoparticles are
added to a sol containing aluminium oxide and said sol is then gelatinized, dried, calcinated and sintered. The invention also relates
to $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains.

(57) Zusammenfassung: Verfahren zur Herstellung von $\text{Al}_2\text{O}_3/\text{SiC}$ -Nanokomposit-Schleifkörnern, wobei ein aluminiumoxidhalti-
ges Sol mit SiC-Nanopartikeln versetzt, anschließend geliert, getrocknet, kalziniert und gesintert wird sowie $\text{Al}_2\text{O}_3/\text{SiC}$ -Nanokom-
posit-Schleifkorn.

Illustrations

[see original drawing]

III. 1. Elementary diagram of the test stand for one-grain scratching

rel scratch cross section
 $\Lambda_{R0}/\Lambda_{R0}$

[see original]

Grinding Conditions.

| | |
|------------------------|-------------|
| Material | 100Cr6 |
| Cutting speed v_c | 30m/s |
| Feed motion a_f | 20 μ m |
| Work piece speed v_w | 0.5 mm/s |
| Coolant | 3% emulsion |

----- cBN
----- Example 4
----- sol/gel corundum
----- melt corundum
----- structure ceramics
(Al₂O₃/5%SiC)

mm scratch length

III. 2: Abrasion curves of Al₂O₃/SiC nanocomposites as compared with some typical abrasive grains

3 / 3

[photograph]

Figure 3

[photograph]

Figure 4

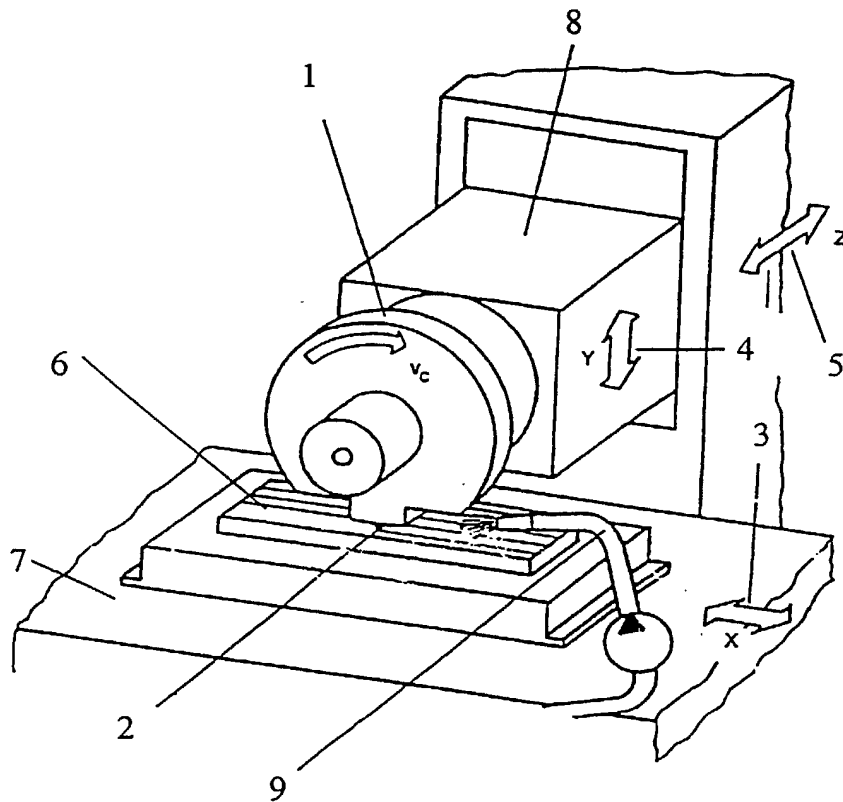
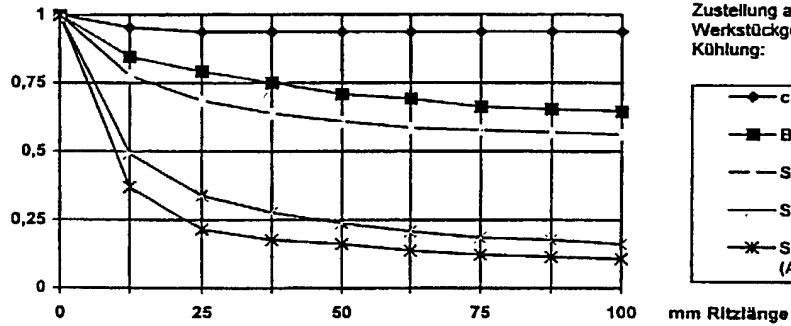
Abbildungen

Abb. 1: Prinzipieller Aufbau des Prüfstandes zum Einkornritzen

bez. Ritzquerschnitt
 A_{Rz}/A_{R0}



Schleifbedingungen:

Werkstoff: 100Cr6
 Schnittgeschwindigkeit v_c : 30 m/s
 Zustellung a_a : 20 μ m
 Werkstückgeschw. v_w : 0,5 mm/s
 Kühlung: 3 % Emulsion

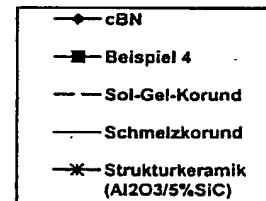


Abb. 2: Verschleißkurven von $\text{Al}_2\text{O}_3/\text{SiC}$ -Nanokomposits im Vergleich zu einigen typischen Schleifkörnungen



FIG. 3



FIG. 4

Please type a plus sign (+) inside this box →



PTO/SB/01 (10-00)

Approved for use through 10/31/2002 OMB 0651-0032
U S Patent and Trademark Office, U S DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number

**DECLARATION FOR UTILITY OR
DESIGN
PATENT APPLICATION
(37 CFR 1.63)**

☒ Declaration
Submitted With Initial
Filing
OR
☐ Declaration
Submitted after Initial
Filing (surcharge
(37 CFR 1.16 (e))
required)

Attorney Docket Number 12707 P04
First Named Inventor Paul Moeltgen et al.

COMPLETE IF KNOWN

Application Number 10/088,849
Filing Date March 21, 2002
Group Art Unit
Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Al2O3/SiC NANOCOMPOSITE ABRASIVE GRAINS, METHOD FOR PRODUCING
THEM AND THEIR USE**

the specification of which (Title of the Invention)

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) **March 21, 2002** as United States Application Number or PCT International

Application Number **10/088,849** and was amended on (MM/DD/YYYY) **March 21, 2002** (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims as amended specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) Country | Priority Not Claimed | Certified Copy Attached? | |
|-------------------------------------|----------------|--|-------------------------------------|--------------------------|-------------------------------------|
| | | | | YES | NO |
| PCT/EP00/09230 199 45 335.7 | PCT Germany | 09/21/2000 09/22/1999 | <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below

| Application Number(s) | Filing Date (MM/DD/YYYY) | <input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto |
|-----------------------|--------------------------|---|
| | | |

[Page 1 of 2]

Burden Hour Statement This form is estimated to take 21 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO Assistant Commissioner for Patents, Washington, DC 20231.

Please type a plus sign (+) inside this box →



PTO/SB/01 (10-00)

Approved for use through 10/31/2002 OMB 0651-0032
U S Patent and Trademark Office, U S DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number

DECLARATION — Utility or Design Patent Application

| | | | | | |
|--|--|--|---|---------------------|---|
| Direct all correspondence to: | | <input checked="" type="checkbox"/> Customer Number or Bar Code Label | 26486 | OR | <input type="checkbox"/> Correspondence address below |
| Name | | | | | |
| Address | | | | | |
| Address | | | | | |
| City | | | State | ZIP | |
| Country | | Telephone | | Fax | |
| I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon | | | | | |
| NAME OF SOLE OR FIRST INVENTOR: | | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | | |
| Given Name Paul | | | Family Name MOELTGEN or Surname | | |
| Inventor's Signature <i>P. Moeltgen</i> | | | Date 14.06.02 | | |
| Residence: City Laufenburg | | State | Country GERMANY | Citizenship GERMANY | |
| Mailing Address c/o TREIBACHER SCHLEIFMITTEL GmbH | | | | | |
| Mailing Address Ferroweg 1 | | | | | |
| City Laufenburg | | State | ZIP 79725 | Country GERMANY | |
| NAME OF SECOND INVENTOR: | | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | | |
| Given Name Pirmin | | | Family Name WILHELM or Surname | | |
| Inventor's Signature <i>P. Wilhelm</i> | | | Date 17.06.02 | | |
| Residence: City Laufenburg-Binzgen | | State | Country GERMANY | Citizenship GERMANY | |
| Mailing Address c/o TREIBACHER SCHLEIFMITTEL GmbH | | | | | |
| Mailing Address Ferroweg 1 | | | | | |
| City Laufenburg | | State | ZIP 79725 | Country GERMANY | |
| <input checked="" type="checkbox"/> Additional inventors are being named on the 1 supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto | | | | | |

Please type a plus sign (+) inside this box ➡

Approved for use through 10/31/2002 OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number

| | |
|--------------------|---|
| DECLARATION | ADDITIONAL INVENTOR(S) Supplemental Sheet Page <u>1</u> of <u>2</u> |
|--------------------|---|

| | | | |
|--|-------|---|-----------------------------|
| Name of Additional Joint Inventor, if any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name <u>Anne Louise Ghislaine</u> | | Family Name or Surname <u>LERICHE</u> | |
| Inventor's Signature <u>[Signature]</u> | | Date <u>23.06.02</u> | |
| Residence: City <u>Soignies</u> | State | Country <u>BELGIUM</u> | Citizenship <u>FRENCH</u> |
| Mailing Address <u>17, rue Ferrer</u> <u>[Signature]</u> | | | |
| Mailing Address | | | |
| City <u>Soignies</u> | State | ZIP <u>7060</u> | Country <u>BELGIUM</u> |
| Name of Additional Joint Inventor, if any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name <u>Christine Marie Renee</u> | | Family Name or Surname <u>KERMEL-KIM</u> | |
| Inventor's Signature <u>[Signature]</u> | | Date <u>24.06.2002</u> | |
| Residence: City <u>Saint Quay Perros</u> | State | Country <u>FRANCE</u> <u>[Signature]</u> | Citizenship <u>FRENCH</u> |
| Mailing Address <u>13, rue Park ar C'hra</u> | | | |
| Mailing Address | | | |
| City <u>St Quay Perros</u> | State | Zip <u>22700</u> | Country <u>FRANCE</u> |
| Name of Additional Joint Inventor, if any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name <u>Georg</u> | | Family Name or Surname <u>GOTTSCAMEL</u> | |
| Inventor's Signature <u>[Signature]</u> | | Date <u>01 July 2002</u> | |
| Residence: City <u>Guttaring</u> | State | Country <u>AUSTRIA</u> | Citizenship <u>AUSTRIAN</u> |
| Mailing Address <u>Mallnerweg 11</u> | | | |
| Mailing Address | | | |
| City <u>Guttaring</u> | State | Zip <u>9334</u> | Country <u>AUSTRIA</u> |

Bureau Hour Statement: This form is estimated to take 21 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U S Patent and Trademark Office, Washington, DC 20231. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO:** Assistant Commissioner for Patents, Washington, DC 20231.

PTO/SB/81 (10-00)
Approved for use through 10/31/2002 OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
to respond to a collection of information unless it displays a valid OMB

Burden Hour Statement: This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any Comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U S Patent and Trademark Office, Washington, DC 20231. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231**

PTO/SB/81 (10-00)
Approved for use through 10/31/2002 OMB 0651-0035
U S Patent and Trademark Office, U S DEPARTMENT OF COMMERCE

| | |
|--|---|
| I hereby appoint: | |
| <input checked="" type="checkbox"/> Practitioners at Customer Number | 26486 |
| OR | |
| <input type="checkbox"/> Practitioner(s) named below: | Place Customer Number Bar Code Label here |

| Name | Registration Number |
|------|---------------------|
| | |
| | |
| | |
| | |

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the Patent and Trademark Office connected therewith.

Please change the correspondence address for the above-identified application to:

☐ The above-mentioned Customer Number.

OR


| | | | | | |
|--|--|-------|--|-----|--|
| <input type="checkbox"/> Firm or Individual Name | | | | | |
| Address | | | | | |
| Address | | | | | |
| City | | State | | ZIP | |
| Country | | | | | |
| Telephone | | Fax | | | |

I am the.

☒ Applicant.

☐ Assignee of record of the entire interest. See 37 CFR 3.71.
Certificate under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

SIGNATURE of Applicant or Assignee of Record

| | |
|-----------|---|
| Name | Pirmin Wilhelm |
| Signature |  |
| Date | 17.06.02 |

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below*.

☒ *Total of 5 forms are submitted

Burden Hour Statement This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any Comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U S Patent and Trademark Office, Washington, DC 20231. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO Assistant Commissioner for Patents, Washington, DC 20231**

Please type a plus sign (+) inside this box

PTO/SB/81 (10-00)
 Approved for use through 10/31/2002 OMB 0651-0035
 U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

POWER OF ATTORNEY OR AUTHORIZATION OF AGENT

| | |
|------------------------|----------------------|
| Application Number | 10/088,849 |
| Filing Date | March 21, 2002 |
| First Named Inventor | Paul Moeltgen et al. |
| Group Art Unit | |
| Examiner Name | |
| Attorney Docket Number | 12707 P04 |

I hereby appoint:

☒ Practitioners at Customer Number

26486

OR

☐ Practitioner(s) named below:

Place Customer
 Number Bar Code
 Label here

| Name | Registration Number |
|------|---------------------|
| | |
| | |
| | |
| | |

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the Patent and Trademark Office connected therewith.

Please change the correspondence address for the above-identified application to.

☐ The above-mentioned Customer Number.

OR

☐ Firm or Individual Name

Address

Address

City

State

ZIP

Country

Telephone

Fax

I am the:

☒ Applicant☐ Assignee of record of the entire interest. See 37 CFR 3.71.

Certificate under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

SIGNATURE of Applicant or Assignee of Record

| | |
|-----------|--------------------------|
| Name | Georg GOTTSCHAMEL |
| Signature | <i>Georg Gottschamel</i> |
| Date | <i>1. July 2002</i> |

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required..

Submit multiple forms if more than one signature is required, see below*

☒ *Total of 5 forms are submitted

Burden Hour Statement. This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any Comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231 DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO Assistant Commissioner for Patents, Washington, DC 20231

10033349 107.1302

Please type a plus sign (+) inside this box

PTO/SB/81 (10-00)
 Approved for use through 10/31/2002 OMB 0651-0035
 U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

POWER OF ATTORNEY OR AUTHORIZATION OF AGENT

| | |
|-------------------------------|-----------------------|
| Application Number | 10/088,849 |
| Filing Date | March 21, 2002 |
| First Named Inventor | Paul Moeltgen, et al. |
| Group Art Unit | |
| Examiner Name | |
| Attorney Docket Number | 12707 P04 |

I hereby appoint

☒ Practitioners at Customer Number

26486

OR

☐ Practitioner(s) named below

Place Customer
 Number Bar Code
 Label here

| Name | Registration Number |
|------|---------------------|
| | |
| | |
| | |
| | |

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the Patent and Trademark Office connected therewith.

Please change the correspondence address for the above-identified application to:

☐ The above-mentioned Customer Number.

OR

☐ Firm or
 Individual Name

Address

Address

City

State

ZIP

Country

Telephone

Fax

I am the:

☒ Applicant.

☐ Assignee of record of the entire interest. See 37 CFR 3.71.

Certificate under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

SIGNATURE of Applicant or Assignee of Record

| | |
|------------------|----------------------------------|
| Name | Christine Marie Renee KERMEL-KIM |
| Signature | <i>ckermel</i> |
| Date | 24.06.2002 |

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below*

☒ *Total of 5 forms are submitted.

Burden Hour Statement This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any Comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS SEND TO: Assistant Commissioner for Patents, Washington, DC 20231

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

POWER OF ATTORNEY OR AUTHORIZATION OF AGENT

| | |
|-------------------------------|-----------------------|
| Application Number | 10/088,849 |
| Filing Date | March 21, 2002 |
| First Named Inventor | Paul Moeltgen, et al. |
| Group Art Unit | |
| Examiner Name | |
| Attorney Docket Number | 12707 P04 |

I hereby appoint.

☒ Practitioners at Customer Number

26486

Place Customer
Number Bar Code
Label here

OR

☐ Practitioner(s) named below:

| Name | Registration Number |
|------|---------------------|
| | |
| | |
| | |
| | |
| | |

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the Patent and Trademark Office connected therewith.

Please change the correspondence address for the above-identified application to:

☐ The above-mentioned Customer Number.

OR

☐ Firm or
Individual Name

Address

Address

City

State

ZIP

Country

Telephone

Fax

I am the:

☒ Applicant.☐ Assignee of record of the entire interest. See 37 CFR 3.71.

Certificate under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

SIGNATURE of Applicant or Assignee of Record

| | |
|------------------|-------------------------------|
| Name | Anne Louise Ghislaine LERICHE |
| Signature | <i>Anne Leriche</i> |
| Date | 23.06.02 |

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required
Submit multiple forms if more than one signature is required, see below*

☒ *Total of 5 forms are submitted

Burden Hour Statement This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any Comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231